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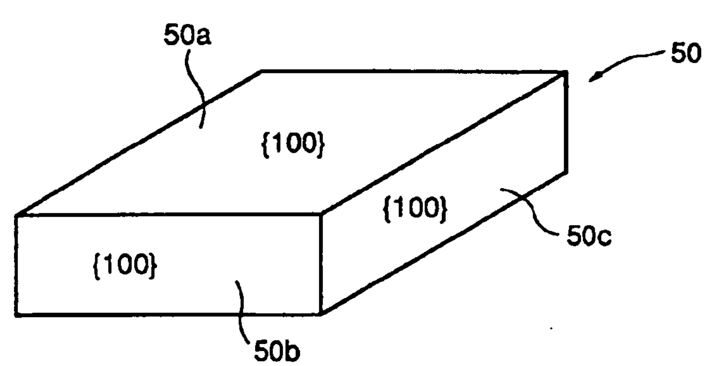
(54) Method and apparatus for producing single-crystalline diamond

(57) An initial single-crystalline diamond base material (50) is prepared from a flat plate having a major surface (50a) and side surfaces consisting of low-index planes for homoepitaxially vapor-depositing single-crystalline diamond on the single-crystalline diamond base material (50), thereby forming single-crystalline diamond having a large area. Holding means (1) for the single-crystalline diamond base material (50) consists of a material hardly forming a compound with carbon, or is coated with such a material. According to this method and this apparatus, single-crystalline diamond can be stably formed on the surfaces of the base material (50). Consequently, single-crystalline diamond of high quality having a large area can be stably produced in a shorter time by either plasma CVD or a thermal filament method.

FIG. 1A



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Description

The present invention relates to a method of and an apparatus for producing single-crystalline diamond through vapor-phase synthesis, and more particularly, it relates to a method of and an apparatus for producing relatively large-sized single-crystalline diamond of at least about 10 mm by 10 mm, which is applied to a cutting tool, a precision tool, a semiconductor material, an electronic component, an optical component or the like.

Diamond, which has many excellent properties such as high hardness, high heat conductivity and transparency, is widely employed as materials for various tools, optical components, semiconductors, electronic components and the like, and its importance is expected to increase in the years ahead.

While naturally produced diamond has been applied to industrial use in the past, artificially synthesized diamond is generally employed at present. In general, relatively large-sized polycrystalline diamond is artificially produced by vapor-phase synthesis such as plasma CVD (chemical vapor deposition) (refer to "Applied Physics", Vol. 55, No. 7, 1986, pp. 640 to 653, for example). In such polycrystalline diamond, however, a polycrystalline diamond layer which is formed on a substrate is so heterogeneous that no sufficiently flat surface is obtained by polishing. In application to a super-precision tool, an optical component or a semiconductor particularly requiring a flat surface, therefore, it is necessary to employ single-crystalline diamond having homogeneous crystal orientations. While such single-crystalline diamond is naturally produced, the output thereof is so small that a method of artificially producing single-crystalline diamond has been studied in general.

With the vapor-phase synthesis technique, single-crystalline diamond is generally produced by plasma vapor deposition of vapor-depositing single-crystalline diamond on a base material with a low- or high-temperature plasma which is generated by mixing at least one carbon source selected from hydrocarbon, carbon oxide, alcohol and acetone with hydrogen, oxygen, water, nitrogen or halogen for preparing source gas and decomposing and activating the source gas with a direct current, a low-frequency alternating current, a high frequency or a microwave, or a thermal filament method of vapor-depositing single-crystalline diamond on a base material with a thermoionic emissive material such as a tungsten filament which is heated to a high temperature. In either method, the single-crystalline diamond can be homoepitaxially grown on a single-crystalline diamond base material or heteroepitaxially grown on a non-diamond base material depending on the type of the employed base material. In case of homoepitaxially growing the single-crystalline diamond, the base material may be prepared by bonding a plurality of single-crystalline diamond base materials which are adjacently arranged in the same plane with each other to attain a large area for mosaic growth (refer to Japanese Patent Laying-Open No. 3-75298 (1991), Diamond and Related Material, No. 4 (1995) pp. 1025 to 1031 etc.).

In the conventional homoepitaxial growth, however, abnormal growth is caused on side surfaces due to growth of twins or secondary nuclei, while transverse spreading is inhibited by polycrystalline diamond growing from a base material holder. In relation to the heteroepitaxial growth, on the other hand, a problem of inconsistency in in-plane orientation is not yet solved although a technique for attaining regular orientations on the upper surface has been developed. In the mosaic growth, inconsistent junctions between the single-crystalline diamond base materials remain as interfaces to cause abnormal growth, and hence the area of the single-crystalline diamond cannot be increased. In order to prevent formation of the interfaces, the angles of the base materials must be completely regularized.

In general, further, the base material holder is prepared from a material such as silicon, silicon carbide or cubic boron nitride readily forming a compound by reaction with carbon, disadvantageously leading to formation of polycrystalline diamond inhibiting growth of single-crystalline diamond in the vicinity of the base material.

An object of the present invention is to provide a method of stably producing single-crystalline diamond having a large area by either plasma CVD or a thermal filament method and an apparatus for producing the same.

In order to attain the aforementioned object, the method of producing single-crystalline diamond according to the present invention is mainly characterized in that a base material having a major surface and side surfaces consisting of low-index planes is employed as a single-crystalline diamond base material for homoepitaxially vapor-depositing single-crystalline diamond on this base material thereby forming single-crystalline diamond having a large area.

The term "low-index planes" is defined as indicating all of {100}, {110} and {111} planes and those forming angles within 5° with respect to these planes, as well as {311}, {331}, {511}, {551} and {711} planes and those forming angles within 1° with respect to these planes in Miller indices.

Thus, the single-crystalline diamond base material is prepared from that having a major surface and side surfaces consisting of low-index planes which are stable in energy, whereby single-crystalline diamond can be stably grown on the surfaces of the base material for forming high-quality single-crystalline diamond having a large area.

In a preferred embodiment of the present invention, single-crystalline diamond is produced under a vapor deposition condition for increasing the vapor deposition rate of the single-crystalline diamond on the low-index planes forming the side surfaces of the single-crystalline diamond base material. Due to selection of such a vapor deposition condition, single-crystalline diamond having

a large area can be formed in a shorter time, for improving production efficiency.

In the single-crystalline diamond base material, the major surface preferably consists of a square plane having an inclination within 5° with respect to {100} planes, and the four side surfaces are preferably prepared from planes having an inclination within 5° with respect to {100} or {110} planes.

The ratio of a vapor deposition rate V<100> in a <100> direction to a vapor deposition rate V<111> in a <111> direction, i.e., a growth rate ratio defined as V<100>/V<111> is employed as an index of the vapor deposition rate of the single-crystalline diamond on the side surfaces of the base material consisting of such low-index planes, and a condition for homoepitaxial growth is decided in response to the plane orientation of the side surfaces of the base material. In more concrete terms, the single-crystalline diamond is grown under a <100> orientation growth condition at a growth rate ratio of at least 1.62, particularly preferably at least $3^{0.5}$, when the side surfaces of the base material are formed by {100} planes. On the other hand, the single-crystalline diamond is grown under a <110> orientation condition at a growth rate ratio of 0.81 to 0.92, particularly preferably $0.5 \times 3^{0.5}$, when the side surfaces are formed by {110} planes, or under a <111> orientation growth condition at a growth rate ratio of not more than 0.64, particularly preferably not more than $3^{-0.5}$, when the side surfaces are formed by {111} planes. When the side surfaces are formed by two plane orientations, the single-crystalline diamond is grown under a condition responsive to either plane orientation. Thus, the growth rate toward this orientation is at the maximum on extensions of the side surfaces to hardly cause abnormal growth, whereby regions including abnormal growth can be limited.

In another preferred embodiment of the present invention, the single-crystalline diamond base material is prepared from that having a major surface consisting of a square plane having an inclination within 5° with respect to {100} planes and four side surfaces consisting of planes having an inclination within 5° with respect to {100} planes, with employment of a vapor deposition condition for most increasing the vapor deposition rate of the single-crystalline diamond with respect to {111} planes.

When such a <111> orientation condition is employed in place of the <110> orientation condition, the thickness of the {110} side surfaces is not gradually reduced with progress of the growth dissimilarly to the case of the <110> orientation condition, whereby single-crystalline diamond base having a larger area can be readily formed.

According to the present invention, the single-crystalline diamond is vapor-deposited on the major surface and the side surfaces of the single-crystalline diamond base material and thereafter cut out by cutting the base material along a plane substantially perpendicular to the major surface so that low-index planes different from the side surfaces before vapor deposition form new side surfaces, thereby removing twins or secondary nuclei abnormally growing during homoepitaxial growth.

In still another preferred embodiment of the present invention, the single-crystalline diamond base material is prepared from that having four side surfaces consisting of planes having an inclination within 5° with respect to {100} planes. In advance of the step of cutting the base material along a plane substantially perpendicular to the major surface for cutting out single-crystalline diamond which is substantially in the form of a rectangular parallelepiped, the inventive method further comprises a step of removing portions between an upper surface and the upper major surface of the single-crystalline diamond base material and between a lower surface and upper ends of inclined surfaces growing from lower sides of the four side surfaces by polishing when upper ends of the inclined surfaces reach the vertical position of the upper major surface of the single-crystalline diamond base material or a preceding stage.

The aforementioned portions are removed by polishing when the upper ends of the inclined surfaces growing from the lower sides of the four side surfaces reach the vertical position of the upper major surface of the single-crystalline diamond base material or in the preceding stage since unnecessary portions are formed if the single-crystalline diamond is continuously grown after the inclined surfaces reach the upper major surface of the single-crystalline diamond base material, against the object of the present invention for quickly forming large-sized single-crystalline diamond.

In order to improve the production efficiency by growing the single-crystalline diamond in portions requiring largest areas, it is preferable to advance to a next step when the inclined surfaces appearing from the lower sides of the four side surfaces reach the upper surface of the single-crystalline diamond base material (to positions shown by broken lines in Fig. 4B).

In a further preferred embodiment of the present invention, the single-crystalline diamond base material is prepared from that having four side surfaces consisting of planes having an inclination within 5° with respect to {110} planes. In advance of the step of cutting the base material along a plane substantially perpendicular to the major surface for cutting out single-crystalline diamond which is substantially in the form of a rectangular parallelepiped, the method further comprises steps of removing a portion between an upper surface formed by growth of the upper major surface of the base material and a plane including edge lines formed by intersection lines between pairs of inclined surfaces, having an angle within 5° with respect to {110} planes, vertically oppositely growing on the four side surfaces respectively, for forming a new growth start major surface consisting of a plane having an inclination within 5° with respect to a {111} plane when the pairs of inclined surfaces grow until the intersection lines therebetween form the edge lines

to disappear growth planes parallel to the four side surfaces or in a preceding stage, then vapor-depositing the single-crystalline diamond on the new growth start major surface, and thereafter removing a portion between the lower surface and the new growth start major surface.

The steps of removing the portion between the upper surface formed by growth of the major surface and the plane including the edge lines when the intersection lines between the pairs of inclined surfaces grow to form the edge lines to disappear the growth planes parallel to the four side surfaces of the single-crystalline diamond base material or in the preceding stage since the sizes of the single-crystalline diamond planes which can be cut out from the single-crystalline diamond base material after the growth are not increased but only polycrystalline diamond portions regarded as defective in the inventive method are increased against the object of the present invention for quickly forming large-sized single-crystalline diamond even if the single-crystalline diamond is continuously grown after the stage of disappearance of the growth planes parallel to the four side surfaces of the single-crystalline diamond base material (the stage grown to the positions shown by broken lines in Fig. 9B). In order to improve the production efficiency by maximizing the area of the single-crystalline diamond which can be cut out from the base material, it is preferable to advance to a next step when the four side surfaces are just disappeared due to the growth of the pairs of inclined surfaces.

The step of cutting out the single-crystalline diamond which is substantially in the form of a rectangular parallelepiped by cutting the base material along the planes substantially perpendicular to the major surface includes a step of cutting out the diamond so that planes having an inclination within 5° with respect to {100} planes form new side surfaces when planes having an inclination within 5° with respect to {100} planes form the side surfaces before cutting, or a step of cutting out the diamond so that planes having an inclination within 5° with respect to {100} planes form new side surfaces when planes having an inclination within 5° with respect to {110} planes form the side surfaces before cutting.

According to the inventive method of producing single-crystalline diamond, single-crystalline diamond having a large area is formed by alternately repeating a step of cutting out single-crystalline diamond having side surfaces consisting of planes having an inclination within 5° with respect to {100} planes before cutting so that planes having an inclination within 5° with respect to {110} planes form new side surfaces and a step of cutting out single-crystalline diamond having side surfaces consisting of planes having an inclination within 5° with respect to {110} planes before cutting so that planes having an inclination within 5° with respect to {100} planes form new side surfaces.

The inventive apparatus for producing single-crystalline diamond enabling excellent implementation of the aforementioned method of producing single-crystalline diamond according to the present invention comprises a reaction vessel, source gas supply means for supplying source gas for vapor-depositing diamond into the reaction vessel, exhaust means for discharging the gas from the reaction vessel and decompressing the same, and base material holding means for holding a single-crystalline diamond base material in the reaction vessel. At least a portion of the base material holding means in the vicinity of a region for receiving the single-crystalline diamond base material consists of a material hardly forming a compound with carbon or is coated with a material hardly forming a compound with carbon.

According to this structure, precipitation of diamond from the base material holding means is suppressed, thereby suppressing formation of polycrystalline diamond inhibiting growth of single-crystalline diamond. Consequently, an excited diamond precursor is hardly caught on the holding means to increase the probability of reaching side surfaces of the base material, whereby single-crystalline diamond having a large area can be further quickly produced.

In such base material holding means, at least the portion in the vicinity of the region for receiving the single-crystalline diamond base material preferably consists of any material selected from copper, platinum, iridium, molybdenum, graphite, gold, silver, nickel and cobalt, or is preferably coated with any of these materials.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings, provided by way of example.

Fig. 1A is a perspective view showing an initial single-crystalline diamond base material having an upper surface of a square {100} plane and side surfaces of {100} planes employed in each Example of the present invention, Fig. 1B is a perspective view showing a shape of the single-crystalline diamond base material shown in Fig. 1A in an intermediate growth stage during prescribed vapor deposition, and Fig. 1C is a perspective view showing a shape of the single-crystalline diamond base material with upper ends of inclined surfaces growing from lower ends of the side surfaces reaching the vertical position of the upper major surface of the initial single-crystalline diamond base material;

Fig. 2A is a perspective view showing a shape of the single-crystalline diamond base material shown in Fig. 1C after removing a portion between a lower surface and the upper ends of the inclined surfaces by polishing, Fig. 2B is a perspective view showing a shape of the single-crystalline diamond base material shown in Fig. 2A after removing a portion between an upper surface and depressed parts on four upper corners by polishing, and Fig. 2C is a plan view showing positions for cutting the single-crystalline diamond base material formed through the step shown in Fig. 2B;

Fig. 3A illustrates the single-crystalline diamond

base material in the intermediate growth stage shown in Fig. 1B as viewed from a side surface, and Fig. 3B is a model diagram for illustrating the change of the shape of the single-crystalline diamond base material from the state shown in Fig. 1B to that shown in Fig. 1C during the growth process as viewed from the side surface;

Fig. 4A is a plan view of the initial single-crystalline diamond base material shown in Fig. 1A, Fig. 4B is a plan view of the single-crystalline diamond base material in the vapor deposition stage shown in Fig. 1B, and Fig. 4C is a plan view showing the single-crystalline diamond base material in the stage before the cutting step shown in Fig. 2C;

Fig. 5A is a perspective view showing an initial single-crystalline diamond base material having an upper surface of a square {100} plane and side surfaces of {110} planes employed in each Example of the present invention, Fig. 5B is a perspective view showing a shape of the single-crystalline diamond base material shown in Fig. 5A in an intermediate growth stage during prescribed vapor deposition, and Fig. 5C is a perspective view showing a shape of the single-crystalline diamond base material in a stage when intersection lines of pairs of inclined surfaces oppositely growing from upper and lower ends of the side surfaces form edge lines;

Fig. 6A is a perspective view showing a shape of the single-crystalline diamond base material after removing a portion between an upper surface of the single-crystalline diamond base material shown in Fig. 5C and a plane including the edge lines formed by the pairs of intersection lines by polishing, Fig. 6B is a perspective view showing a shape of the single-crystalline diamond base material shown in Fig. 6A after performing prescribed vapor deposition from a growth start surface defined by the upper surface of the single-crystalline diamond base material, and Fig. 6C is a perspective view showing a shape of the single-crystalline diamond base material after removing a portion between a lower surface formed through the step shown in Fig. 6B and the growth start surface by polishing, with cut positions in a subsequent cut-out step;

Fig. 7A illustrates the single-crystalline diamond base material in the intermediate growth stage shown in Fig. 5B as viewed from a side surface, and Fig. 7B is a model diagram for illustrating the change of the shape of the single-crystalline diamond base material from the state shown in Fig. 5B to that shown in Fig. 5C during the growth process as viewed from the side surface;

Fig. 8A is a plan view of the initial single-crystalline diamond base material shown in Fig. 5A, Fig. 8B is a plan view of the single-crystalline diamond base material in the vapor deposition stage shown in Fig. 5B, and Fig. 8C is a plan view of the single-crystalline diamond base material before the cut-out step shown in Fig. 6C;

Figs. 9A to 9C are plan views for illustrating preferable ranges of growth thicknesses of single-crystalline diamond toward side surfaces of base materials in stages of cutting the base materials, and among these figures, Fig. 9A is a plan view in case of cutting the base material along cut lines 12 forming a square when the growth thickness toward a {100} plane in a <100> direction is about 22 % of the initial length of each side of the base material for cutting out diamond in the form of a square pole, Fig. 9B is a plan view in case of cutting the base material along cut lines 12 forming a square on corner portions when the growth thickness toward a {100} plane in a <100> direction is about 22 % of the initial length of each side of the base material similarly to the case shown in Fig. 9A for cutting out diamond in the form of an octagonal pole, and Fig. 9C is a plan view in case of cutting the base material along cut lines 12 forming a square when the vapor deposition thickness toward a {100} plane in a <100> direction is about 50 % of the initial length of each side of the base material for cutting out diamond in the form of a square pole;

Fig. 10 is a model diagram showing a microwave CVD apparatus employed for an experiment in Example 1 of the present invention; and

Fig. 11 is a model diagram showing a thermal filament CVD apparatus for diamond vapor-phase synthesis employed for an experiment in Example 2 of the present invention.

(Example 1)

Fig. 10 is a model diagram showing a microwave CVD apparatus for diamond vapor-phase synthesis employed for an experiment in Example 1 of the present invention. In the microwave CVD apparatus shown in Fig. 10, a microwave generation part consisting of a microwave power source 4, an isolator, tuners 5 and the like generates microwaves, which are directed to a plunger 10 through a waveguide 6. The waveguide 6 is provided on its intermediate position with a silica tube 7 serving as a reaction vessel, which is provided with a source gas inlet port 9 and an outlet port 8 on its upper and lower portions respectively. A base material holder 1 is arranged on a position of the silica tube 7 intersecting with the waveguide 6, so that a base material 2 is set on this base material holder 1.

A base material (hereinafter referred to as a prime base material) 50 shown in Figs. 1A and 4A is prepared from single-crystalline diamond of at least 0.5 mm in thickness having an upper surface 50a of a square {100} plane and side surfaces 50b and 50c of {100} planes and set on the base material holder 1, which is made of molybdenum, of the microwave CVD apparatus for homoepitaxially growing diamond under a <100> preferential orientation growth condition at a growth rate ratio of about $3^{0.5}$ with methane-hydrogen mixed gas having methane concentration of 10 ± 0.5 % while maintaining the pressure in the reaction vessel 7 at 140 ± 5 Torr and the temperature of the prime base material 50 at 1000 ± 10°C. Thus, diamond grows as shown in Figs. IB, 3A and 4B so that inclined surfaces 51 appear from lower portions of the side surfaces 50b and 50c of the prime

base material 50 while abnormal growing parts 11 (see Fig. 4B) and depressed parts 52 appear on four corners and upper corner portions of an upper surface respectively.

Thereafter the diamond further grows with no abnormal growth on extensions of the {100} side surfaces 50b and 50c as shown in Fig. 1C, so that an upper end of each inclined surface 51 reaches a position shown by a broken line in Fig. 3B, i.e., the position of the upper major surface 50a of the prime base material 50. In this stage, the portion between a lower surface and the upper ends of the inclined surfaces 51 shown by broken lines in Fig. 2A is removed by polishing, and thereafter the portion shown by broken lines in Fig. 2B, i.e., between an upper surface and lower ends of the depressed parts 52 on the four corners of the upper surface 50a is polished to disappear the depressed parts 52, thereby forming a diamond substrate 53 which is in the form of a rectangular parallelepiped including the abnormal growing parts 11, as shown in Figs. 2C and 4C. This substrate 53 is cut along cut lines 12 shown in Figs. 2C and 4C with a YAG laser beam, thereby forming a flat single-crystalline diamond substrate (prime base material) 60 having an upper surface 60a consisting of a square {100} plane and four side surfaces 60b and 60c consisting of {110} planes, as shown in Figs. 5A and 8A.

Then, diamond is grown under a <110> preferential orientation growth condition at a growth rate ratio of $0.5 \times 3^{0.5}$ with methane-hydrogen mixed gas having methane concentration of 3 ± 0.5 % while maintaining the pressure in the reaction vessel 7 at 140 ± 5 Torr and the temperature of the prime base material 60 at 1050 ± 10°C, whereby the diamond grows as shown in Figs. 5B and 7A. Due to the aforementioned step, inclines surfaces 61 and 62 appear as shown in Figs. 5B and 8B from upper and lower ends of the four side surfaces 60b and 60c of the prime base material 60 shown in Figs. 5A and 8A. While abnormal growing parts 11 appear on four corners of the prime base material 60, the diamond grows with no abnormal growth on extensions of the {110} side surfaces 60b and 60c.

When the diamond grows until intersection lines between the inclined surfaces 61 and 62 appearing from the upper and lower ends of the side surfaces 60b and 60c form edge lines 63 as shown in Fig. 5C, a portion between an upper surface and a plane including the edge lines 63 is removed by polishing so that a surface having no abnormal growth appears as a front surface, thereby forming a substrate 64 having a growth start surface 64a shown in Fig. 6A. Then, the <100> preferential orientation growth condition is applied to homoepitaxially grow diamond on the growth start surface 64a, thereby forming a single-crystalline diamond layer 65 on the substrate 64, as shown in Fig. 6B. Thereafter the substrate 64 located under the single-crystalline diamond layer 65 is removed by polishing from a lower surface, to obtain the flat single-crystalline diamond layer 65 including the abnormal growing parts 11 on four corners as shown in Figs. 6C and 8C. This single-crystalline diamond layer 65 is cut with a YAG laser beam along cut lines 12 shown in Fig. 6C, thereby forming single-crystalline diamond having an upper surface 50a and four side surfaces 50b and 50c all consisting of {100} planes and including no abnormal growing parts as shown in Fig. 1A. Flat single-crystalline diamond having a large area can be obtained by repeating the aforementioned steps.

While the <110> preferential orientation growth condition is employed in the homoepitaxy step shown in Fig. 5A with the single-crystalline substrate 60 serving as a prime base material in this Example, the object of the present invention can also be attained by employing a <111> preferential orientation growth condition for most increasing the growth rate in <111> directions in place of the <110> preferential orientation growth condition, for the following reason:

It is generally known that isolated grains of diamond formed by homoepitaxy from points are generally formed by two types of planes, i.e., {100} and {111} planes. This is because the diamond mainly grows toward the {100} and {111} planes in <100> and <111> directions while relatively hardly growing toward the remaining planes. As understood from the fact that the growth rate ratio serving as an index specifying each orientation growth direction is defined as the ratio of the vapor deposition rate V<100> in the <100> direction to the vapor deposition rate V<111> in the <111> direction, therefore, it is known that the growth rates toward the remaining low-index planes are decided by the large-small relation between the growth rates in the <100> and <111> directions.

When the <110> preferential orientation growth condition is applied to the prime base material 60 shown in Fig. 5A as described above, the growth rate ratio is $0.5 \times 3^{0.5}$ and the vapor deposition rate in the <111> direction is higher than that in the <100> direction, whereby the growth of the diamond is remarkably influenced by the vapor deposition in the <111> direction. Therefore, the diamond grows into the shape shown in Fig. 7A after vapor deposition, and the thickness of each {110} plane is gradually reduced as shown in Fig. 7B, to reduce the thickness of each region causing no abnormal growth. When the <111> preferential orientation growth condition is applied to the prime base material 60 shown in Fig. 5A in place of the <110> preferential orientation condition, on the other hand, it is possible to grow the diamond without reducing the thickness of each region causing no abnormal growth. Namely, the object of the present invention can also be attained by applying the <111> orientation growth condition dissimilarly to the <110> orientation growth condition for most increasing the growth rate toward the side surfaces in case of homoepitaxially growing diamond on a prime base material having a major surface of a {100} plane and side surfaces of {110} planes.

A method of obtaining single-crystalline diamond having the largest area in the cutting step with the YAG laser beam in this Example is now described. The step of cutting the prime base material 50 or 60 with the YAG laser beam along the cut lines 12 described with reference to Figs. 2C and 4C or 6C and 8C is carried out when single-crystalline diamond grows on the side surfaces 50b and 50c or 60b and 60c of the single-crystalline diamond base material 50 or 60 in a thickness of not more than 50 % of the initial length of each side. If the prime base material 50 or 60 is cut when the single-crystalline diamond grows on the side surfaces 50b and 50c or 60b and 60c in a thickness exceeding 50 % of the initial length of each side, portions including no abnormal growth are removed in a large amount against the object of the present invention for quickly forming single-crystalline diamond having a larger area. In order to maximize the production efficiency, however, it is preferable to cut out the single-crystalline diamond when growing on the side surfaces 50b and 50c or 60b and 60c of the prime base material 50 or 60 in a thickness of about 50 % of the initial length of each side.

Figs. 9A to 9C illustrate preferable ranges of growth thicknesses of single-crystalline diamond toward side surfaces of base materials in stages of cutting the base materials. First, consider the case of cutting the base material into the form of a square pole with no abnormal growing parts 11 when the growth thickness toward each {110} plane in a <100> direction is about 22 % of the initial length of each side of the base material along cut lines 12 forming respective sides of a square, i.e., along {110} planes in four corners. In this case, the area sl of a triangle formed on each corner of diamond which is cut out from the initial base material is substantially identical to the area s2 of each growing part remaining as a new corner part after cutting, whereby the plane area of the cut base material is substantially equal to that of the base material in consequence. If the base material is cut along the {110} planes on four corners into the form of a square pole while removing the abnormal growing parts when the growth thickness toward the {100} planes in the <100> directions is not in excess of about 22 % of the initial length of each side of the base material, therefore, the plane area of the cut base material is merely identical to or smaller than that of the initial base material. In case of cutting out diamond in the form of a flat square, therefore, it is necessary to cut the base material when the growth thickness toward the {100} planes in the <100> directions is at least in excess of about 22 % of the initial length of each side of the base material.

Even if the growth thickness toward the {100} planes in the <100> directions is not in excess of about 22 % of the initial length of each side of the base material, however, it is possible to obtain a single-crystalline diamond base material having a larger plane area than the initial one by cutting the base material along the lines 12, i.e., along {110} planes on the corner portions for cutting out diamond into the form of an octagonal pole including {100} and {110} planes on its side surfaces while removing abnormal growing parts 11, as shown in Fig. 9B.

In case of cutting the base material along cut lines 12 forming a square, i.e., along {110} planes on four corners into the form of a square pole while removing abnormal growing parts 11 when the growth thickness toward {100} planes in <100> directions is about 50 % of the initial length of each side of the base material, a new base material having a plane area of about twice the initial one is obtained as understood from Fig. 9C, and the efficiency is most improved in consideration of the yield of single-crystalline diamond from which the abnormal growing parts 11 are removed. When the base material is cut after the diamond grows with in excess of 50 %, however, single-crystalline diamond parts are excessively removed for removing the abnormal growing parts 11 and the obtained plane area is merely identical to that in the case of 50 %. Therefore, the diamond is preferably cut out by cutting the base material along the {110} planes on the four corners when the growth thickness toward the {100} planes in the <100> directions is not more than 50 % of the initial length of each side of the base material, and it is most optimum to cut out the diamond when the growth thickness is 50 %.

(Example 2)

Example 2 of the present invention for vapor-phase synthesizing single-crystalline diamond with application of a thermal filament method is now described.

Fig. 11 is a model diagram showing a thermal filament CVD apparatus for diamond vapor-phase synthesis employed for an experiment. In the thermal filament CVD apparatus shown in Fig. 11, a reaction vessel 21 is provided with an inlet port 22 and an outlet port 23 for source gas. A tungsten filament 25 is arranged in the reaction vessel 21, and an ac power source 24 feeds a current for red-heating the tungsten filament 25. A base material holder 27 of molybdenum is arranged under the tungsten filament 25, for receiving a single-crystalline diamond base material 26. An inlet port 28 and an outlet port 29 for cooling water are provided for supplying cooling water to a lower portion of the base material holder 27 which is heated to a high temperature by the red-heated tungsten filament 25.

The single-crystalline diamond base material 26 is prepared from the single-crystalline diamond base material (prime base material) 50 of at least 0.5 mm in thickness having the upper surface 50a of a square {100} plane and the side surfaces 50b and 50c of {100} planes as shown in Figs. 1A and 4A and set on the base material holder 27 of molybdenum provided in the aforementioned thermal filament CVD apparatus for homoepitaxially growing diamond under a <100> preferential orientation growth condition at a growth rate ratio of about $3^{0.5}$ with methane-hydrogen mixed gas having

methane concentration of 1.3 % while maintaining the pressure in the reaction vessel 21 at 100 Torr and the temperature of the prime base material 50 at 850°C, whereby the diamond grows as shown in Figs. 1B, 3A and 4B so that inclined surfaces 51 appear from lower portions of the side surfaces 50b and 50c of the prime base material 50 while abnormal growing parts 11 (see Fig. 4B) and depressed parts 52 appear on four corners and upper corner portions of an upper surface respectively.

Thereafter the diamond further grows with no abnormal growth on extensions of the {100} side surfaces 50b and 50c as shown in Fig. IC, so that an upper end of each inclined surface 51 reaches the position shown by the broken line in Fig. 3B, i.e., the position of the upper major surface 50a of the prime base material 50. In this stage, the portion between a lower surface and the upper ends of the inclined surfaces 51 shown by broken lines in Fig. 2A is removed by polishing, and thereafter the portion shown by broken lines in Fig. 2B, i.e., between the upper surface and lower ends of the depressed parts 52 on the four corners of the upper surface is polished to disappear the depressed parts 52, thereby forming a diamond substrate 53 which is in the form of a rectangular parallelepiped including the abnormal growing parts 11, as shown in Figs. 2C and 4C. This substrate 53 is cut along cut lines 12 shown in Figs. 2C and 4C with a YAG laser beam, thereby forming a flat single-crystalline diamond substrate (prime base material) 60 having an upper surface 60a consisting of a square {100} plane and four side surfaces 60b and 60c consisting of {110} planes, as shown in Figs. 5A and 8A.

Then, diamond is grown under a <110> preferential orientation growth condition at a growth rate ratio of 0.5 x $3^{0.5}$ with methane-hydrogen mixed gas having methane concentration of 1.2 % while maintaining the pressure in the reaction vessel 27 at 100 Torr and the temperature of the prime base material 60 at 850°C, whereby diamond grows as shown in Figs. 5B and 7A. Due to the aforementioned step, inclines surfaces 61 and 62 appear as shown in Figs. 5B and 8B from upper and lower ends of the four side surfaces 60b and 60c of the prime base material 60 shown in Figs. 5A and 8A. While abnormal growing parts 11 appear on four corners of the prime base material 60, the diamond grows with no abnormal growth on extensions of the {110} side surfaces 60b and 60c.

When the diamond grows until intersection lines between the inclined surfaces 61 and 62 appearing from the upper and lower ends of the side surfaces 60b and 60c form edge lines 63 as shown in Fig. 5C, a portion between an upper surface and a plane including the edge lines 63 is removed by polishing so that a surface having no abnormal growth appears as a front surface, thereby forming a substrate 64 having a growth start surface 64a shown in Fig. 6A. Then, the <100> preferential orientation growth condition is applied to homoepitaxially grow diamond on the growth start surface 64a, thereby forming a single-crystalline diamond layer 65 on the substrate 64, as shown in Fig. 6B. Thereafter the substrate 64 located under the single-crystalline diamond layer 65 is removed by polishing from a lower surface, to obtain the flat single-crystalline diamond layer 65 including the abnormal growing parts 11 on four corners as shown in Figs. 6C and 8C. This single-crystalline diamond layer 65 is cut with a YAG laser beam along cut lines 12 shown in Fig. 6C, thereby forming single-crystalline diamond having an upper surface 50a and four side surfaces 50b and 50c all consisting of {100} planes and including no abnormal growing parts as shown in Fig. 1A. Flat single-crystalline diamond having a large area can be obtained by repeating the aforementioned steps.

Also in this Example, the object of the present invention can be attained by applying the <111> preferential orientation growth condition dissimilarly to the <110> preferential orientation growth condition for most increasing the growth rate toward the side surfaces in case of homoepitaxially growing diamond on a prime base material having a major surface of a {100} plane and side surfaces of {110} planes similarly to Example 1, as a matter of course.

While the plane orientations of the major surface and the side surfaces of the prime base material, the surfaces grown by vapor deposition and the cut planes in the cutting step are formed by {100}, {110} and {111} planes in each Example, the surfaces may not necessarily coincide with such plane orientations but the object of the present invention can be attained when the plane orientations of these surfaces are within the range included in the aforementioned definition of the low-index planes.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

Claims

1. A method of producing single-crystalline diamond by synthesizing single-crystalline diamond on a single-crystalline diamond base material (50, 60) from a vapor phase,

   said single-crystalline diamond base material (50, 60) being prepared from that having a major surface and side surfaces consisting of low-index planes.

2. A method in accordance with claim 1, employing such a vapor deposition condition that a vapor deposition rate for single-crystalline diamond on said low-index planes forming said side surfaces of said

single-crystalline diamond base material (50, 60) is higher than that toward all plane orientations appearing in the remaining portions.

3. A method in accordance with claim 1 or claim 2, wherein said single-crystalline diamond base material (50, 60) is prepared from that having a major surface (50a, 60a) consisting of a square plane having an inclination within 5° with respect to a {100} plane and four side surfaces (50b, 50c, 60b, 60c) consisting of planes having an inclination within 5° with respect to {100} or {110} planes, for applying a <100> plane orientation condition with methane concentration of at least 8 % under a substrate temperature of not more than 1000°C when said side surfaces are formed by {100} planes while applying a <110> plane orientation condition when said side surfaces are formed by {110} planes.

4. A method in accordance with claim 1 or claim 2, wherein said single-crystalline diamond base material (60) is prepared from that having a major surface consisting of a square plane having an inclination within 5° with respect to a {100} plane and four side surfaces (60b, 60c) consisting of planes having an inclination within 5° with respect to {110} planes for employing a <111> orientation condition with methane concentration of not more than 1.5 % under a substrate temperature of at least 1100°, at a vapor deposition rate of said single-crystalline diamond with respect to a {111} plane orientation being higher by at least $3^{0.5}$ times as compared with that toward a <100> direction.

5. A method in accordance with any one of claims 1 to 4, including a step of cutting said single-crystalline diamond base material (50, 60) at least along a plane (12) substantially perpendicular to said major surface so that low-index planes being different from said side surfaces before vapor deposition form new side surfaces after vapor-depositing single-crystalline diamond on said major surface (50a, 60a) and said side surfaces (50b, 50c, 60b, 60c) of said single-crystalline diamond base material (50, 60), thereby cutting out single-crystalline diamond.

6. A method in accordance with any one of claims 1 to 3, wherein said single-crystalline diamond base material (50) is prepared from that having four side surfaces (50b, 50c) consisting of planes having an inclination within 5° with respect to {100} planes,
said method further comprising steps of:

removing a portion between a lower surface and upper ends of inclined surfaces (51) growing from lower sides of said four side surfaces (50b, 50c) when said upper ends of said inclined surfaces (51) reach the vertical position of upper said major surface (50a) of said single-crystalline diamond base material (50) or in a preceding stage, and
grinding an upper surface,
in advance of a step of cutting said single-crystalline diamond base material (50) along a plane being substantially perpendicular to said major surface (50a) for cutting out single-crystalline diamond being substantially in the form of a rectangular parallelepiped.

7. A method in accordance with any one of claims 1, 2 or 4, wherein said single-crystalline diamond base material (60) is prepared from that having four side surfaces (60b, 60c) consisting of planes having an inclination within 5° with respect to {110} planes,
said method further comprising steps of:

removing a portion between an upper surface being formed by growth of upper said major surface and a plane including edge lines (63) being formed by intersection lines of pairs of inclined surfaces (61, 62), having an inclination within 5° with respect to {111} planes, vertically oppositely growing on respective said four side surfaces (60b, 60c), when said intersection lines of said pairs of inclined surfaces (61, 62) grow to form said edge lines (63) to disappear growth planes being parallel to said four side surfaces or in a preceding stage thereby forming a new growth start major surface (64a) consisting of a plane having an inclination within 5° with respect to a {100} plane,
vapor-depositing single-crystalline diamond on said new growth start major surface (64a), and
removing a portion between a lower surface and said new growth start major surface (64a), in advance of a step of cutting said single-crystalline diamond base material (60) along a plane being substantially perpendicular to said major surface (60a) for cutting out single-crystalline diamond being substantially in the form of a rectangular parallelepiped.

8. The method of producing single-crystalline diamond in accordance with claim 5, wherein said step of cutting said single-crystalline diamond base material along said plane being substantially perpendicular to said major surface for cutting out single-crystalline diamond being substantially in the form of a rectangular parallelepiped includes a step of:

cutting out said single-crystalline diamond so that planes having an inclination within 5° with respect to {110} planes form new side surfaces when planes having an inclination within 5° with respect to {100} planes form said side surfaces before cutting, or cutting out single-crystalline

diamond so that planes having an inclination within 5° with respect to {100} planes form new side surfaces when planes having an inclination within 5° with respect to {110} planes form said side surfaces before cutting.

9. The method of producing single-crystalline diamond in accordance with claim 8, alternately repeating a step of cutting out single-crystalline diamond having side surfaces consisting of planes having an inclination within 5° with respect to {100} planes before cutting so that planes having an inclination within 5° with respect to {110} planes form new side surfaces and a step of cutting out single-crystalline diamond having side surfaces consisting of planes having an inclination within 5° with respect to {110} planes before cutting so that planes having an inclination within 5° with respect to {100} planes form new side surfaces.

10. An apparatus for producing single-crystalline diamond for synthesizing single-crystalline diamond on a single-crystalline diamond base material (2, 26) from a vapor phase, said apparatus comprising:

a reaction vessel (7, 21);
source gas supply means for supplying source gas for vapor-depositing diamond into said reaction vessel (7, 21);
exhaust means for discharging said gas from said reaction vessel (7, 21) and decompressing the same; and
substrate holding means (1, 27) for holding said single-crystalline diamond base material in said reaction vessel (7, 21),
at least a portion of said base material holding means (1, 27) in the vicinity of a region for receiving said single-crystalline base material consisting of a material hardly forming a compound with carbon or being coated with a material hardly forming a compound with carbon.

11. The apparatus for producing single-crystalline diamond in accordance with claim 10, wherein at least said portion of said base material holding means (1, 27) in the vicinity of said region for receiving said single-crystalline base material (2, 26) consists of any material among copper, platinum, iridium, molybdenum, graphite, gold, silver, nickel and cobalt, or is coated with any of these materials.

12. A method as claimed in any one of claims 1 to 9, further including the step of incorporating the single-crystalline diamond in a cutting tool, a precision tool, a semiconductor material, an electronic component or an optical component.

FIG. 1A

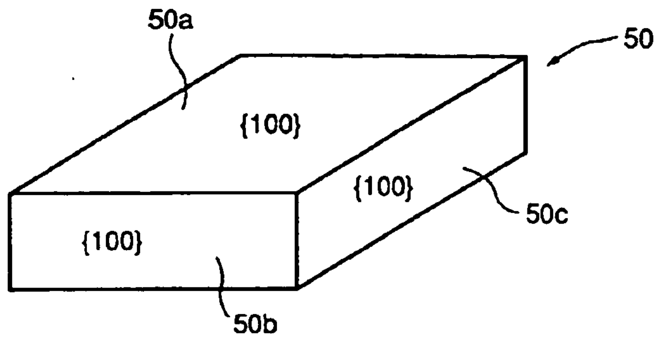


FIG. 1B

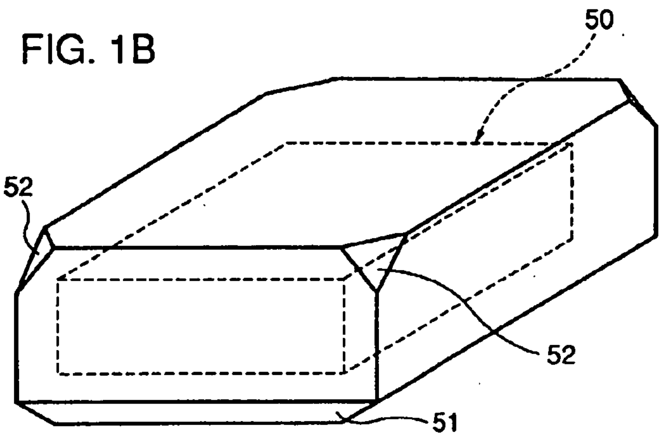


FIG. 1C

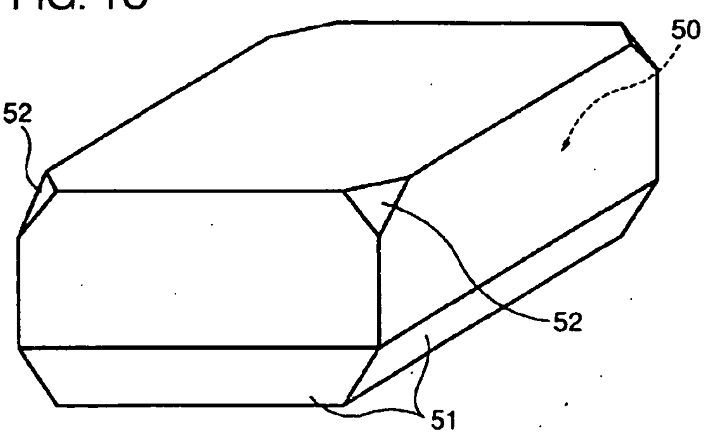


FIG. 2A

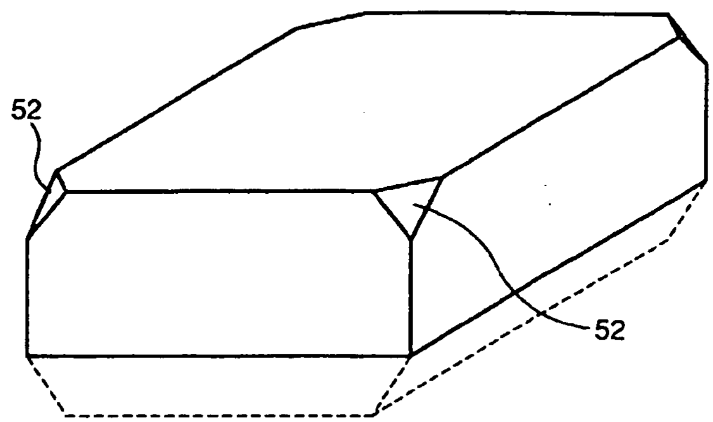


FIG. 2B

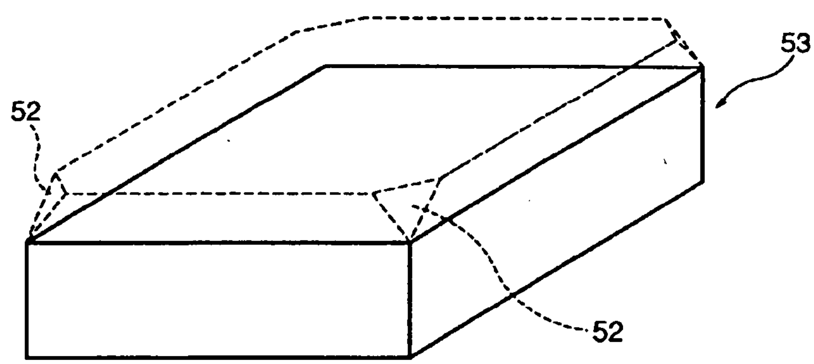


FIG. 2C

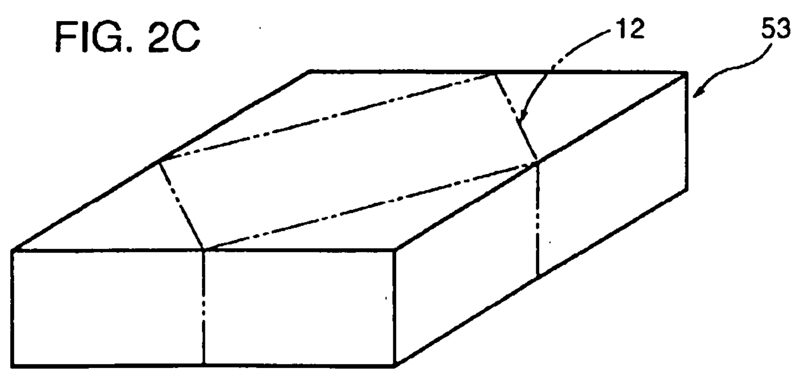


FIG. 3A

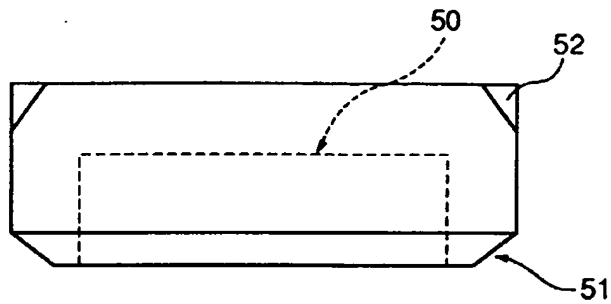


FIG. 3B

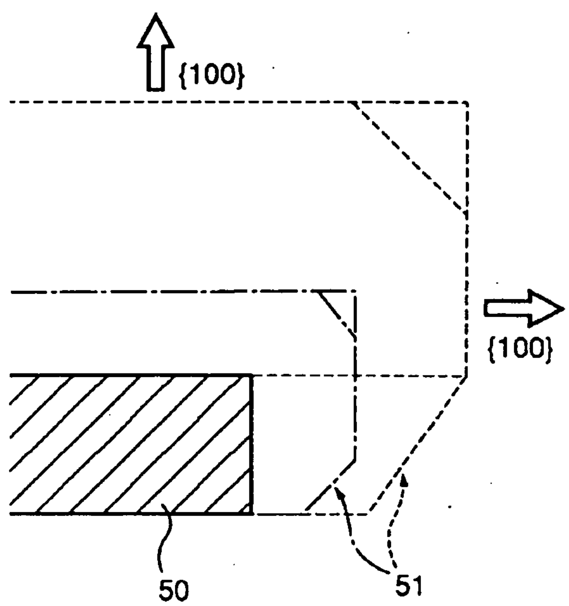


FIG. 4A

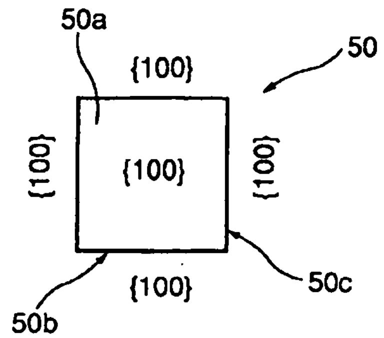


FIG. 4B

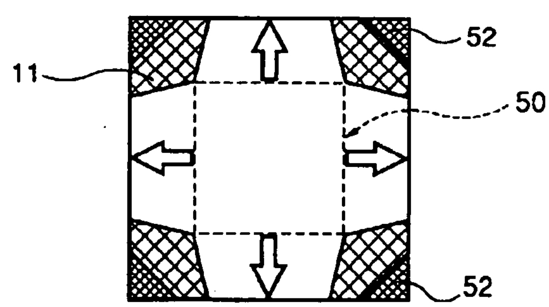


FIG. 4C

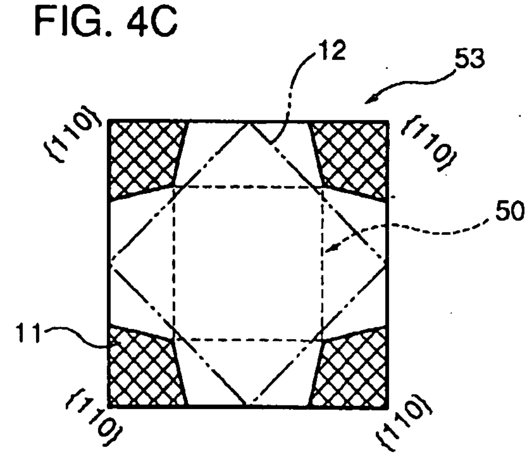


FIG. 5A

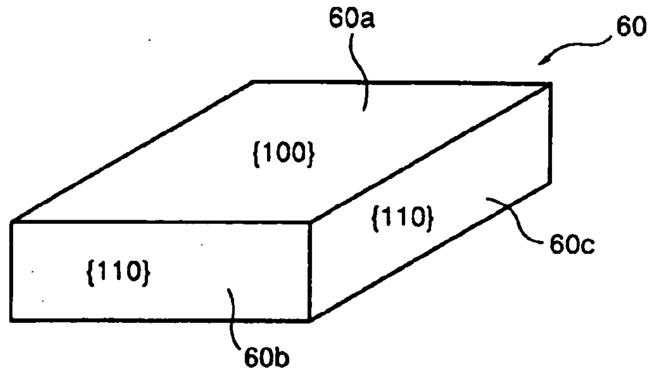


FIG. 5B

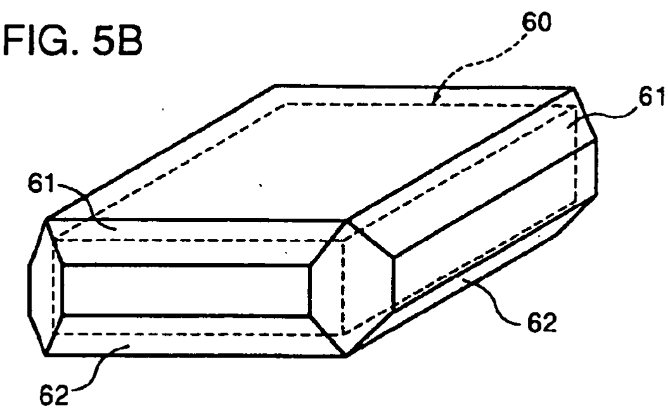


FIG. 5C

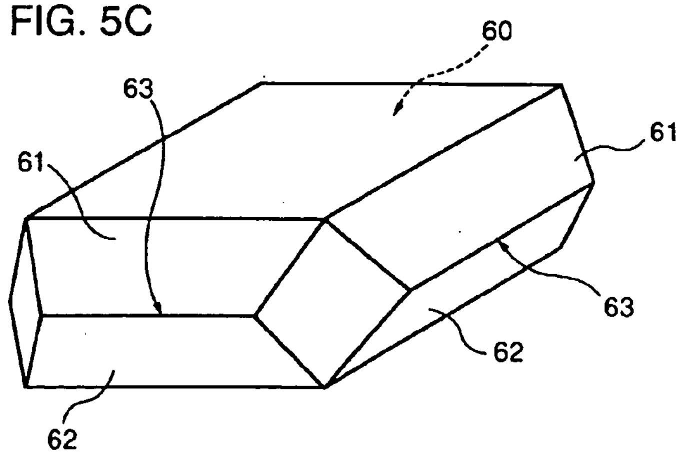


FIG. 6A

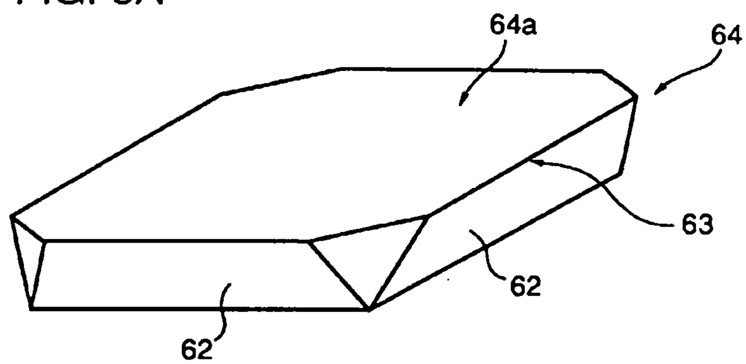


FIG. 6B

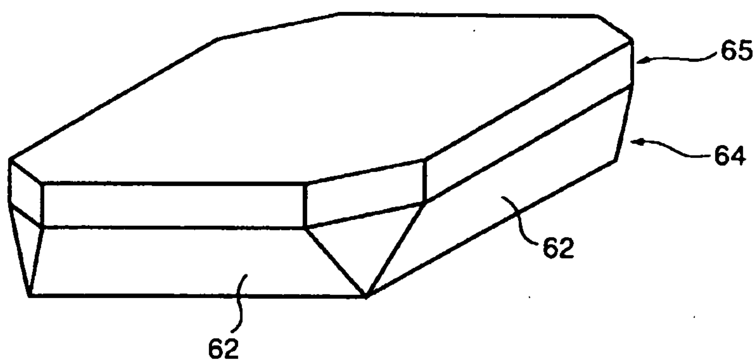


FIG. 6C

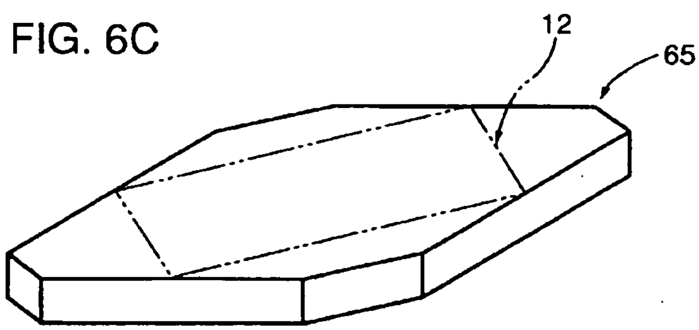


FIG. 7A

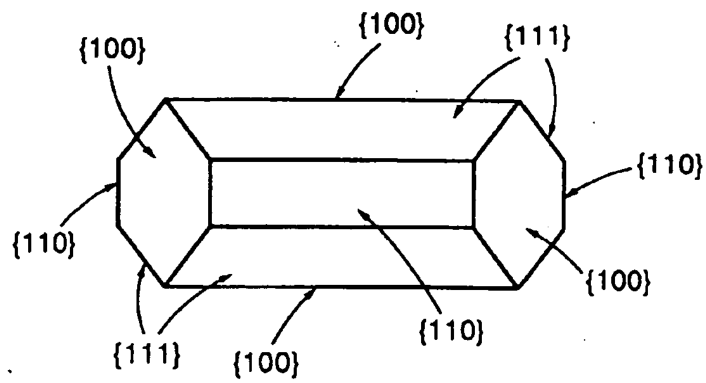


FIG. 7B

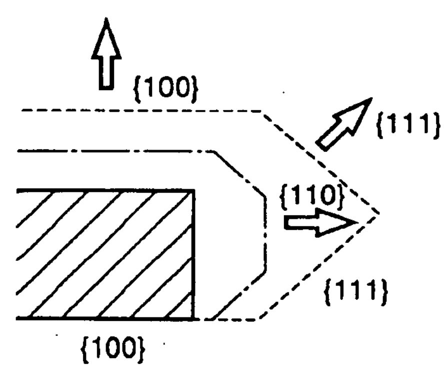


FIG. 8A

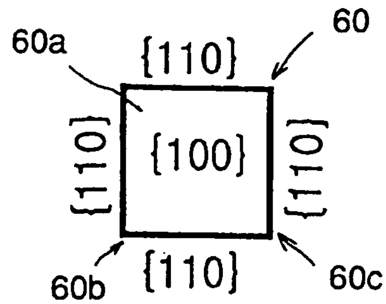


FIG. 8B

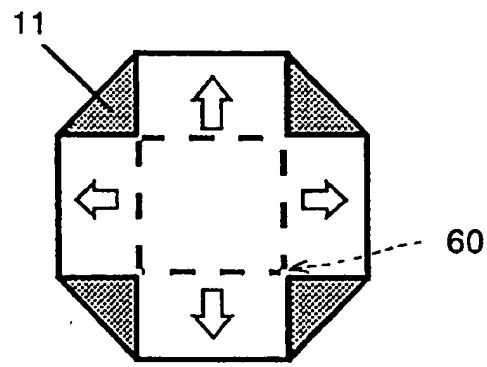


FIG. 8C

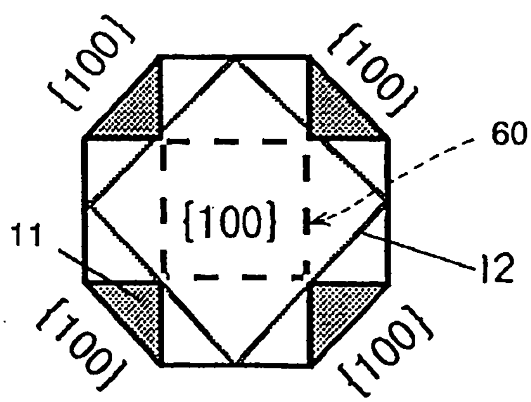


FIG. 9A

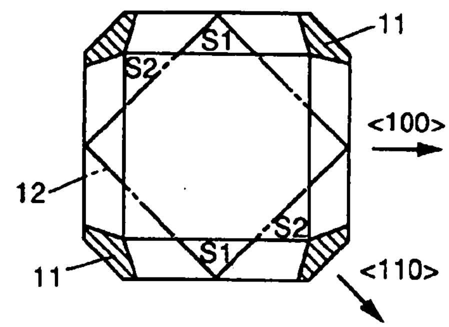


FIG. 9B

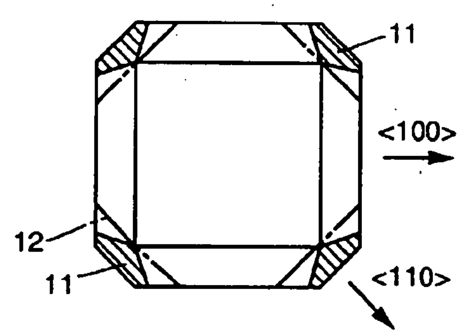


FIG. 9C

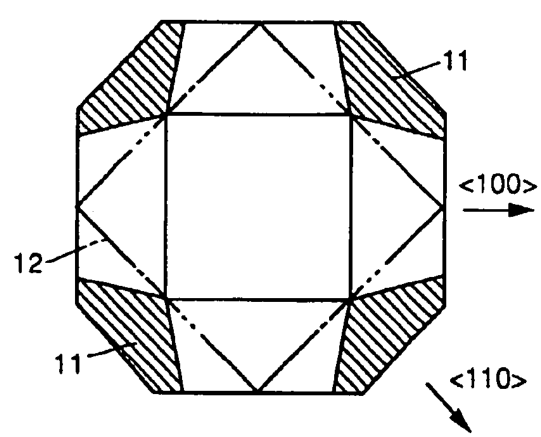


FIG. 10

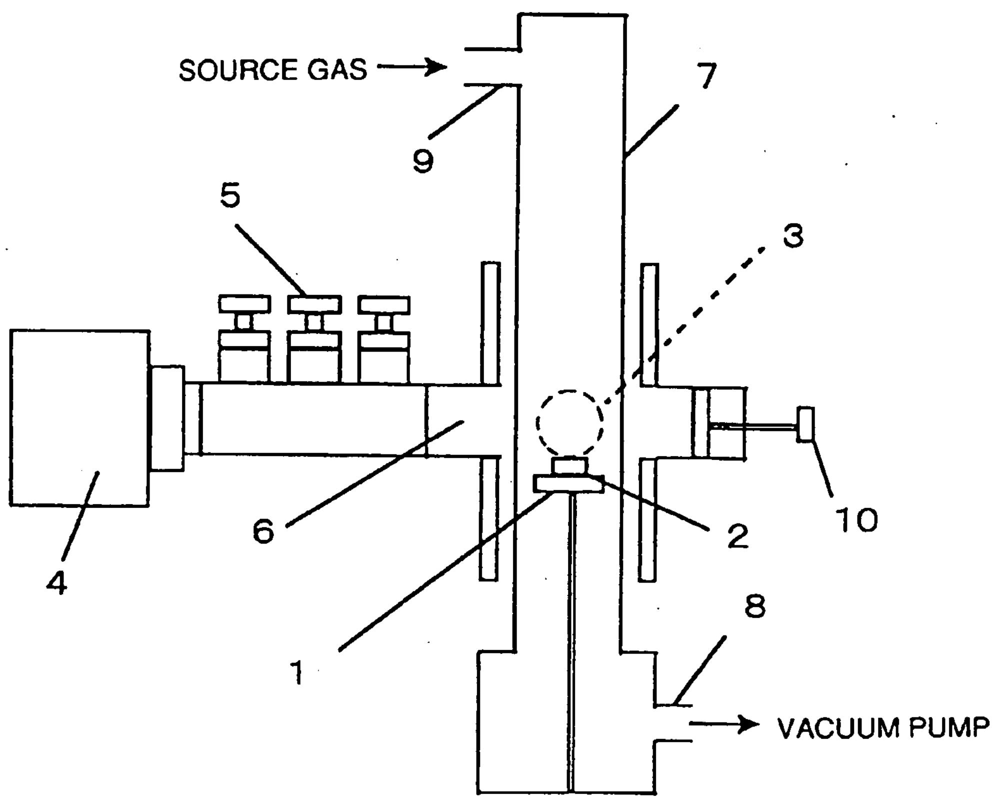
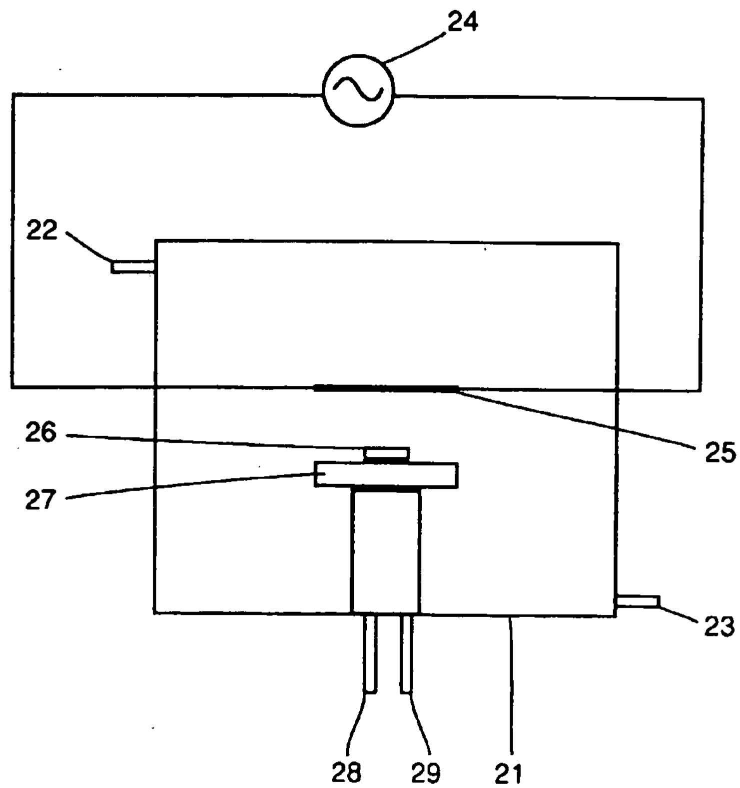


FIG. 11



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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 2982

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 589 464 A (SUMITOMO ELECTRIC INDUSTRIES) 30 March 1994 * page 9, line 23 - line 32; example 1 *	1,2,4	C30B25/02 C30B25/20 C30B29/04
X	SHIOMI H ET AL: "EPITAXIAL GROWTH OF HIGH QUALITY DIAMOND FILM BY THE MICROWAVE PLASMA-ASSISTED CHEMICAL-VAPOR-DEPOSITION METHOD" JAPANESE JOURNAL OF APPLIED PHYSICS, vol. 29, no. 1, PART 01, 1 January 1990, pages 34-40, XP000102172 * page 34, right-hand column, last paragraph - page 33 *	1-3	
X	DATABASE WPI Section Ch, Week 8922 Derwent Publications Ltd., London, GB; Class E36, AN 89-161661 XP002071595 & JP 01 103 994 A (SUMITOMO ELECTRIC IND CO) * abstract *	1,2	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C30B
X	DATABASE WPI Section Ch, Week 8922 Derwent Publications Ltd., London, GB; Class E36, AN 89-161660 XP002071596 & JP 01 103 993 A (SUMITOMO ELECTRIC IND CO) * abstract *	1,2	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	11 September 1998	Killaan, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 2982

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	MAEDA H ET AL: "Determination of diamond 100 and 111 growth rate and formation of highly oriented diamond film by microwave plasma-assisted chemical vapor deposition" JOURNAL OF MATERIALS RESEARCH, DEC. 1995, MATER. RES. SOC, USA, vol. 10, no. 12, ISSN 0884-2914, pages 3115-3123, XP002071594 ---		
X	EP 0 630 994 A (SUMITOMO ELECTRIC INDUSTRIES) 28 December 1994 * page 7, line 26 - line 34; examples 2,3 * ---	10,11	
X	CHU C J ET AL: "Growth kinetics of (100), (110), and (111) homoepitaxial diamond films" APPLIED PHYSICS LETTERS, 21 SEPT. 1992, USA, vol. 61, no. 12, ISSN 0003-6951, pages 1393-1395, XP002077253 * page 1393, right-hand column, paragraph 1 * ---	10,11	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
X	CATLEDGE S A ET AL: "Morphology and quantitative nitrogen impurity measurements in homoepitaxial chemical vapor deposited diamond" THIN FILMS - STRUCTURE AND MORPHOLOGY. SYMPOSIUM, THIN FILMS - STRUCTURE AND MORPHOLOGY. SYMPOSIUM, BOSTON, MA, USA, 2-6 DEC. 1996, 1997, PITTSBURGH, PA, USA, MATER. RES. SOC, USA, pages 635-640, XP002077254 * page 636, paragraph 1-3 * --- -/--	10,11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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Application Number
EP 98 30 2982

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	HARTSELL M L ET AL: "Growth of diamond films on copper" JOURNAL OF MATERIALS RESEARCH, APRIL 1994, USA, vol. 9, no. 4, ISSN 0884-2914, pages 921-926, XP002077255 * page 921-922, paragraph II * -----	10,11	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	11 September 1998	Kiliaan, S

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